



pHe Measurements in Anhydrous Ethanol Fuel by Using Commercial Electrodes

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Overview

- Introduction
- Objectives
- Materials and Methods
- Results
- Conclusions

PROALCOOL (National Alcohol Program):

- ⇒ created in 1975 by the Brazilian Government
- ⇒ to produce alcohol-based fuel to decrease the effects on the balance of payments
- ⇒ anhydrous ethanol was used mixed with gasoline
- ⇒ hydrated form as automotive fuel
- ⇒ to give rise to a new renewable energy source

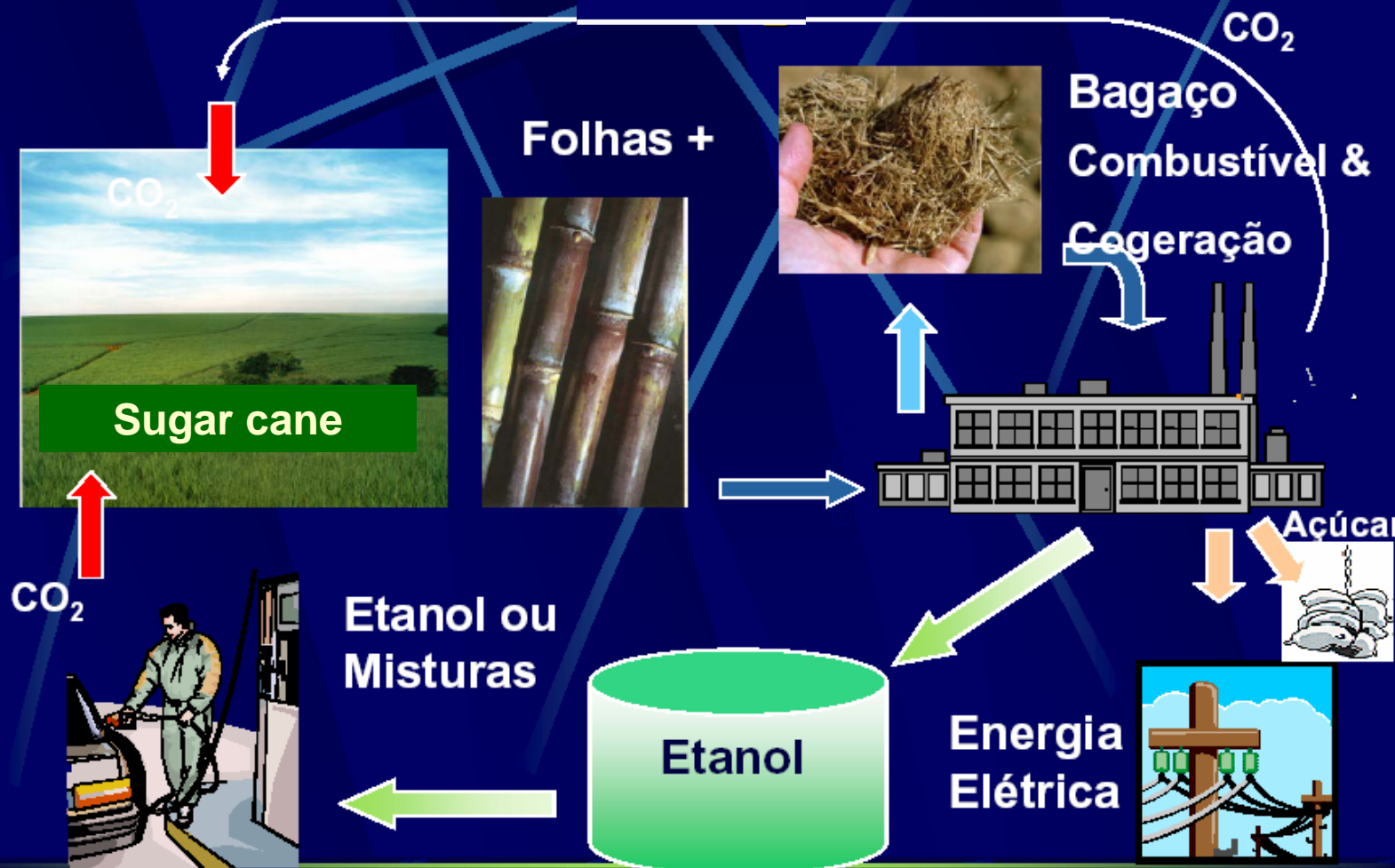


ADVANTAGES:

- ⇒ use of alcohol as fuel to minimize an economic problem
- ⇒ environmental advantages such as elimination of lead as an additive to gasoline
- ⇒ ethanol reduces the emissions of SO₂, CO and hydrocarbons
- ⇒ its use contributes to the reduction of the amount of carbon in the atmosphere.

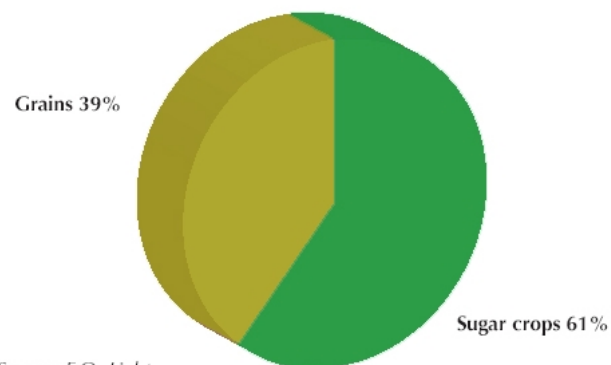


Sugar cane: energy, sugar and capture of CO₂



World Fuel Ethanol

World fuel ethanol production by feedstock



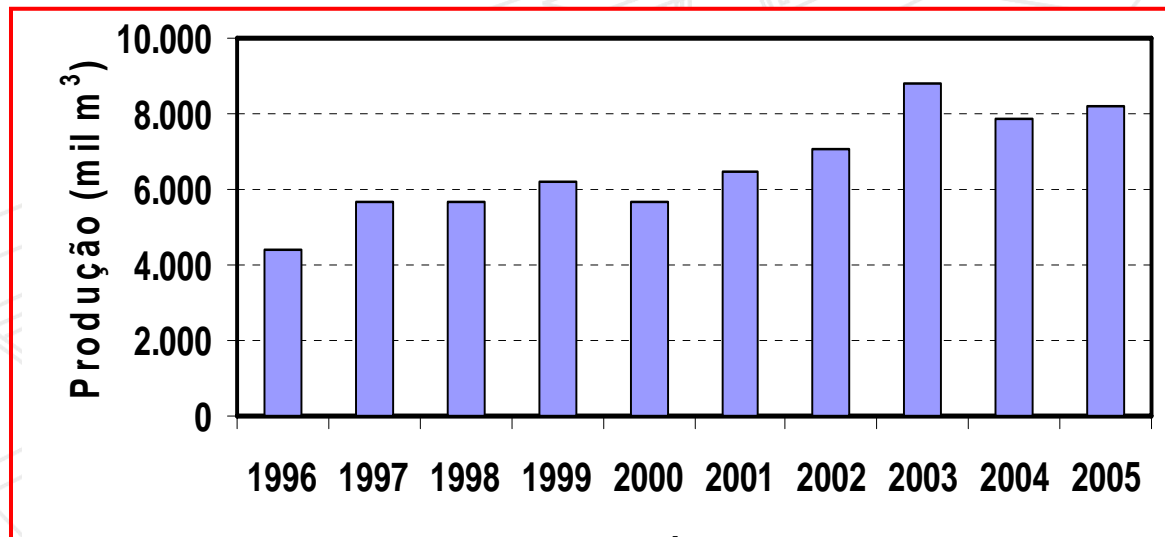
Source F.O. Licht

World Fuel Ethanol



Bioethanol's origin in renewable sugar cane and various cereal crops which are able to reduce carbon in the atmosphere, and is the major factor that contributes to reducing the global warming

Production of Anhydrous Ethanol Fuel in Brazil*



2004 ⇒ Brazil was the first country that had a futures contract on the stock exchange (NYBOT) for anhydrous ethanol ⇒ “commodities”

International market ⇒ specification of ethanol is relevant !

*<http://www.anp.gov.br/doc/anuario2006/T4.2.xls>



- The National Agency of Petroleum, Natural Gas and Biofuels (ANP) is responsible for the control of the quality of biofuels in Brazil. It regulates the limits for several parameters in biofuels, and specifically the pH measurement, according to the ABNT Standard 10891 (2006), “Determination of pH of hydrated ethyl alcohol”.
- pHe is one of the parameters specified in the American Standard, using the ASTM Standard D 6423-99 (2004) “Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol and Fuel Ethanol (ED75-ED85)”.

- pH measurement is important due to the corrosive effect on vehicle engines.
- Because of the difficulty in measuring the pH value in non-aqueous solutions, INMETRO has focused its attention on the need for accurate and reliable measurements through the work for developing and producing Certified Reference Material (CRM) for Anhydrous Ethanol Fuel.





The aim of this work is to present the results of the studies of pH measurements in Anhydrous Ethanol Fuel using 4 different commercial electrodes:

- the influence of variation in temperature
- conditions of stirring of the sample

pHe measurements:

- CRM pH 4.005 (*Inmetro*) and CRM pH 6.865 (*Radiometer*)
- pH meter (*Metrohm*) coupled with different electrodes:
Orion Sure-flow and *Mettler Toledo* (internal solution: $\text{KCl } 3 \text{ mol.L}^{-1}$)
Digimed and *Metrohm* (internal solution: LiCl saturated in ethanol)
- Thermostatic bath (0.13 °C stability) (*Marconi*)
- Pt 100 ($U = 0.25 \text{ }^{\circ}\text{C}$; $k = 2$; $\text{CL} = 95\%$) (*Metrohm*)
- Magnetic stirrer (*Metrohm*)



Orion Sure-Flow Electrode

- Representative samples were taken from a Brazilian producer



- A preliminary study was made of pHe measurements, adapting the procedures described in the ABNT and ASTM Standards

Standard ASTM D 6423-99 (2004)

- Procedure for determining the strength of acidity of the fuel with a high ethanol (pHe) content
- Level of ethanol (75 – 85 %)
- pHe is not directly related to pH in aqueous solutions
- pHe = f (composition of fuel, degree of stirring, time electrode is immersed in solution)
- Measurement temperature → $(22 \pm 2) ^\circ\text{C}$; specific pHe electrode (Orion) and pH meter
- Measurement time: → 30s
- Electrode regeneration: → pH 7.0 and cleaning after 10 measurements (acid and alkaline solutions)

Standard ABNT 10891 (2006)

- Hydrated ethyl alcohol
- Use of combined glass electrode system silver/silver chloride → KCl 3 Mol.L⁻¹ aqueous solution (reference electrolyte → LiCl 3 Mol.L⁻¹ alcoholic solution (electrolyte measurement) and pH meter
- pH 4.00 and pH 6.86 CRMs
- Low stirring → sample and electrode
- Measurement temperature → $(20 \pm 2) ^\circ\text{C}$
- Measurement time → 2 min
- pH is measured (?) → pHe no (?)

Procedure

The pH meter with 2 CRMs should be checked every time it is used to guarantee the correctness of pHe measurements

The electrode is cleaned with deionized water every time a pHe measurement is taken

After 3 pHe measurements,
the glass electrode was regenerated with
 1 mol.L^{-1} HCl solution alternating with 1 mol.L^{-1} NaOH solution

The study of the homogeneity of the sample is notable for being one of the most important factors to assure the maintenance of the physicochemical properties of the material studied.



Factorial Planning 2 levels: 2^2

Factorial 2^2 for electrodes A and B		
Variable	Negative Level	Positive Level
Temperature (°C)	20	25
Electrode	Electrode A	Electrode B
Factorial 2^2 for electrodes C and D		
Variable	Negative Level	Positive Level
Temperature (°C)	20	25
Electrode	Electrode C	Electrode D

Homogeneity of the Sample

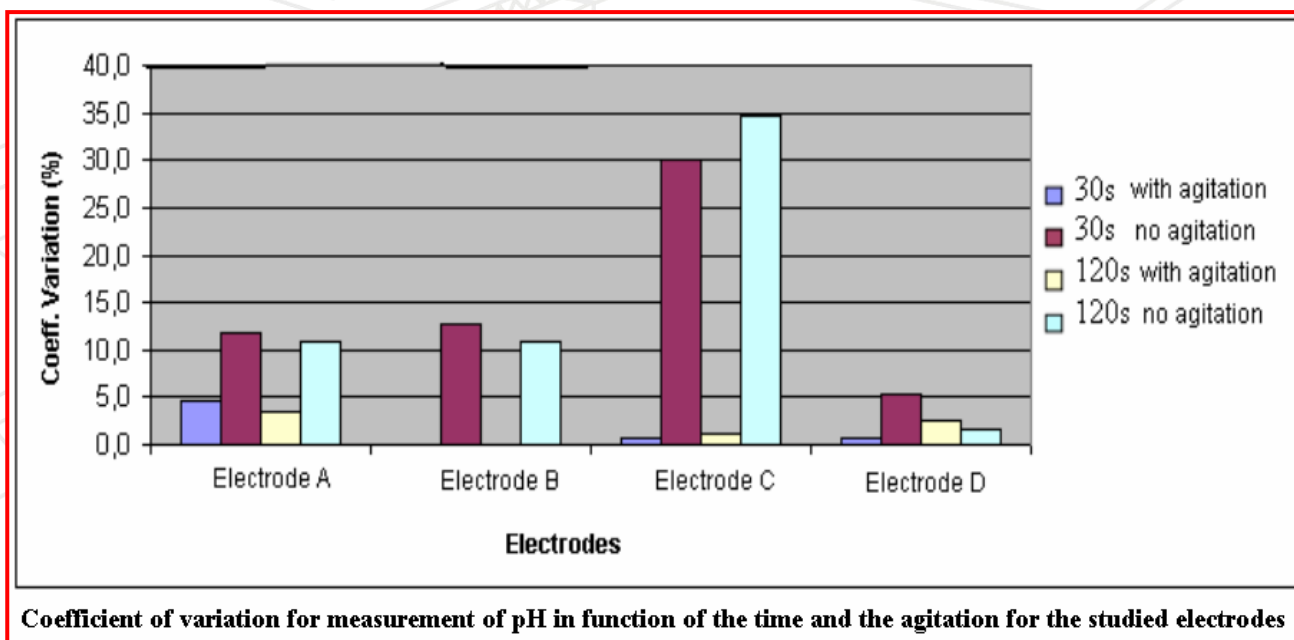
Results from measurements of the homogeneity studies							
Date	Measurements						
09/14/06	5.150	4.566	4.528	4.877	4.130	4.420	4.729
09/15/06	4.572	4.192	4.587	5.607	5.436	4.526	4.155
09/19/06	4.990	4.604	4.677	4.261	5.266	3.920	4.899

Variance Analysis for homogeneity of the anhydrous fuel alcohol						
Source	Degrees of freedom	Sum of squares	Mean square	F_{calc}	p-value	F_{tab}
Between groups	6	1.178779	0.196463159	1.010	0.45719	2.848
Within groups	14	2.722914	0.194493857			
Total	20	3.901693				

$F_{calculated}$: **1.010** is less than $F_{tabulated}$: **2.848** → Sample is homogeneous

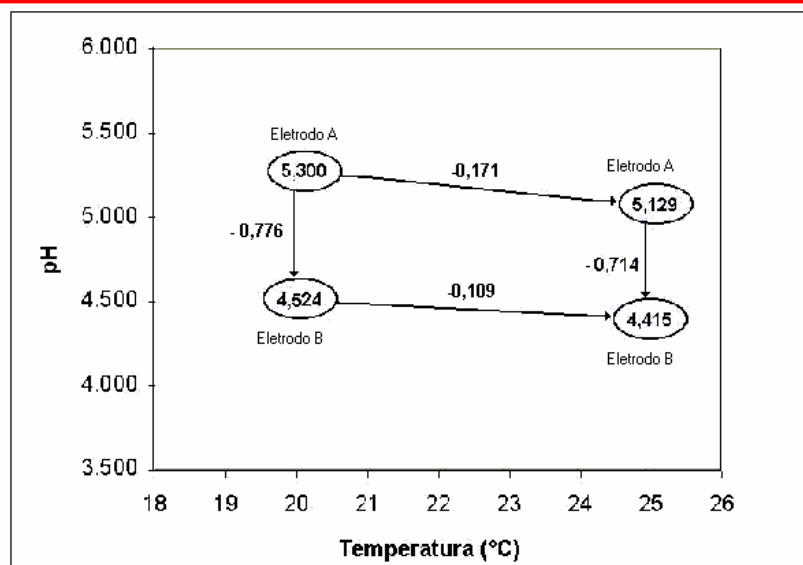
Preliminary Results ($T = 22\text{ }^{\circ}\text{C}$)

Selected conditions: time and stirring of the sample



Planning of Experiments: Electrodes A and B

Results of planning of experiments of factorial 2^2 for Electrodes A and B							
	Temperature (°C)	Electrode	pH		Mean	Standard deviation	Variance
1	20	A	5.169	5.432	5.300	0.1856	0.03445
2	25	A	4.950	5.308	5.129	0.2527	0.0639
3	20	B	4.050	4.998	4.524	0.6699	0.4488
4	25	B	4.000	4.830	4.415	0.5872	0.3448



Interpretation of results in function of temperature em electrodes A and B
(The values of the vertices of quadrilateral are the medium values of pH)

Effects of Factorial Planning 2² : Electrodes A and B

Effects of the factorial 2 ² for electrodes A and B	
	Estimate ± Standard effect error
Total Mean	4.842 ± 0.165
Main Effects	
Temperature	-0.14 ± 0.33
Electrode	-0.75 ± 0.33
Interaction Effects	
Temperature <i>versus</i> Electrode	0.03 ± 0.33

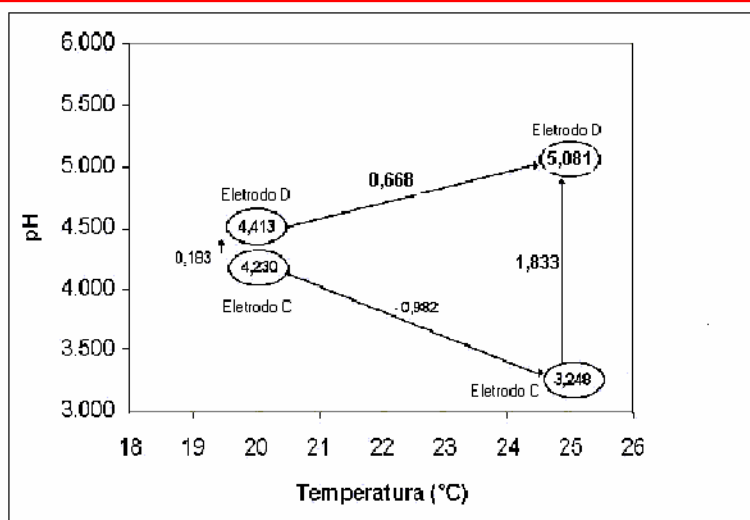
Significant effect, with CL = 95%, if the absolute value is over
 $t_4 (t\text{-student, 4 df}) \times s (\text{standard error}) = 2.776 \times 0.33 = 0.9$

None of them were over 0.9 ⇒ There is no significant difference between the pH measurements performed with electrodes A and B under the proposed conditions

Planning of Experiments: Electrodes C and D

Results of planning of experiments of factorial 2^2 for electrodes C and D

	Temperature (°C)	Electrode	pH		Mean	Standard deviation	Variance
1	20	C	3.437	5.023	4.230	1.121118	1.256905
2	25	C	3.238	3.257	3.248	0.013435	0.00018
3	20	D	3.491	5.334	4.413	1.303198	1.698325
4	25	D	4.939	5.224	5.081	0.201525	0.040613



Interpretação dos resultados em função da temperatura e dos eletrodos C e D
(Os valores dos vértices do quadrilátero são os valores médios de pH)

Effects of Factorial Planning 2^2 : Electrodes C and D

Effects of the factorial 2^2 for electrodes C and D	
	Estimate \pm Standard effect error
Total Mean	4.243 \pm 0.305
Main Effects	
Temperature	-0.16 \pm 0.61
Electrode	1.01 \pm 0.61
Interaction Effects	
Temperature <i>versus</i> Electrode	0.83 \pm 0.61

Significant effect, with CL = 95%, if the absolute value is over than t_4
(*t-student*, 4 df) \times *s* (standard error) = $2.776 \times 0.61 = 1.7$

None of them were over 1.7 \Rightarrow There is no significant difference between the pH measurements performed with electrodes C and D under the proposed conditions

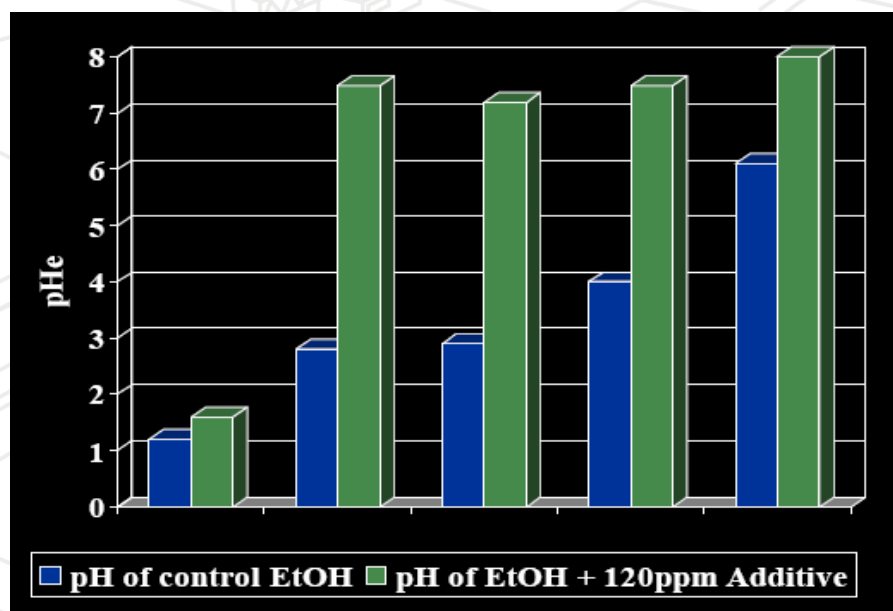
Uncertainty of pHe Measurement with Electrode A

<i>Source</i>	<i>Estimate</i>	<i>ust</i>	<i>Sens. Coeff.</i>	<i>Contribution</i>
<i>pH (S1)</i>	4,005	0,005	0,405644	0,002028221
<i>pH (S2)</i>	7,013	0,005	0,594356	0,002971779
<i>E(S1)</i>	174,600	1,16	0,006957315	0,008046181
<i>E(S2)</i>	-0,8	1,22	0,010193958	0,01246073
<i>E(X)</i>	70,4	10,88	-0,01715127	-0,1866801
<i>Temperature</i>	25	0,05	0,047	0,00235
				u_c 0,187
k=2 (95%)				U 0,375

pHe: 5.129 ± 0.375 (k = 2; CL = 95%)

Additives*

To increase the ethanol pHe value
⇒ According to ASTM



*In: "The European Alternatives Fuel Market and the Role of Fuel Additives",
Simon Mulqueen, *Biofuels Conference*, Greece, 2007



- With the preliminary studies of pHe measurements in anhydrous ethanol fuel using 4 different commercial electrodes, the best results were achieved when the conditions for the experiment were established with measurement times at every 30 s and stirring of the solution, since in those conditions the smallest coefficients of variation were obtained for the pHe value in the sample.
- According to the results obtained in this work, it can be concluded that all of the electrodes studied at 20 °C and 25 °C, with measurement times at every 30 s and with stirring, proved adequate for the measurement of pHe. So, there is no significant difference among the pHe values presented.



- It is worth pointing out that, in this study, the pHe measurements in alcohol solution have no relationship with the pH value obtained from an aqueous solution, since there is a lack of scientific research in this field.
- This study contributes to a better understanding of the pHe measurements in alcohol solutions, providing reliability in pHe measurements, which will be necessary in further developments of CRM for anhydrous ethanol fuel.

- [1] L.R. Lima, A.A. Marcondes, “Álcool Carburante uma Estratégia Brasileira”, Curitiba, UFPR, 2002.
- [2] <http://www.ambientebrasil.com.br/composer.php3base=/natural/index.html&conteúdo=/natural/clima.html>, acessado em outubro de 2006.
- [3] C. Baird, “Química Ambiental”, trad. Maria Angeles Lobo Recio e Luiz Carlos Marques Carrera, 2ª. edição, Porto Alegre, Bookman, 2002.
- [4] <http://www.biodieselbr.com/energia/alcool/etanol.htm>, acessado em outubro de 2006.
- [5] http://www.scielo.br/scielo.phpscript=sci_arttext&pid=S_0100-40422006000100014, acessado em outubro de 2006.
- [6] “Reference materials – General and statistical principles for certification”, ISO GUIDE 35, 2006.
- [7] Vocabulário Internacional de Termos Fundamentais e Gerais de Metrologia – VIM, Portaria Inmetro 029 de 1995, 3ª edição, Rio de Janeiro, 2003.
- [8] American Society for Testing and Materials Standards ASTM Standard Test Method for Determination of pH of Ethanol, Denatured Fuel Ethanol and Fuel Ethanol, D 6423-99, 2004.
- [9] Álcool etílico hidratado - Determinação do pH, ABNT NBR 10891, 2006.
- [10] I. C. S, Fraga, M. A. Getrouw, “A Importância das Medições de pH em Soluções Aquosas”, Apostila de Curso, São Paulo, Enqualab 2002.
- [11] B. B., Neto, R. Bruns, E. Scarmino, “Como fazer Experimentos, Pesquisa e Desenvolvimento na Ciência e na Indústria, 2ª. edição, Campinas, UNICAMP, 2003.
- [12] R. Bruns, “Planejamento e Otimização de Experimento”, Apostila de Curso, Inmetro, 2005.
- [13] I. Kuselman, A. Shenhar, “Uncertainty in Chemical Analysis and Validation of the Analytical Method: Acid Value Determination in Oils”, Accreditation and Quality Assurance, v2, pp.180-185, 1997.
- [14] J. C. V. Oliveira, P. R. G. Couto, “Estimativa de Incerteza na Análise Química”, Convênio Inmetro/UFRJ, Escola de Química, Maio 2001.
- [15] Guia para a Expressão da Incerteza de Medição, 3ª. edição Brasileira em Língua Portuguesa, Rio de Janeiro, ABNT/Inmetro, 2003.



Thank you very much

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